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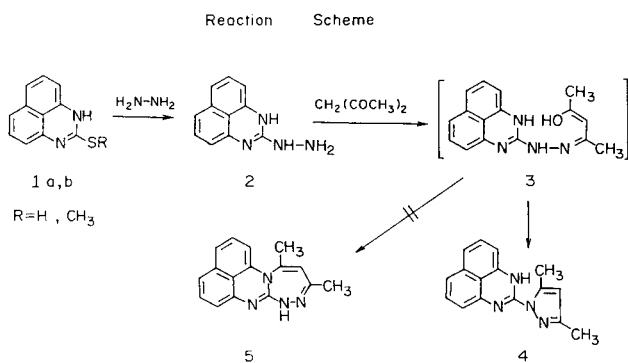
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Received August 4, 1983

Heating 2-hydrazinoperimidine (**2**) with acetylacetone in absolute ethanol gave exclusively 2-(3,5-dimethyl-1-pyrazolyl)perimidine (**4**) via a [2 + 3] cyclization. The possible [4 + 3] condensate, 3,5-dimethyl-1*H*-1,2,4-triazepino[4,3-*a*]perimidine (**5**) was not produced. Spectral analyses were applied to the structure elucidation of the products.

J. Heterocyclic Chem., **21**, 911 (1984).

The compound 2-mercaptoperimidine (**1a**), as it might be readily obtained from 1,8-diaminophthalene by treating with carbon disulfide in excellent yield (95%) [1], has become an important starting material for the synthesis of a variety of condensed perimidine derivatives [1-7]. Hydrolytic cleavage of the C-S bond of **1a** or its *S*-methylated derivative **1b** with hydrazine hydrate might convert it to another versatile intermediate 2-hydrazinoperimidine (**2**). Significantly, **2** underwent cyclocondensation with appropriate carboxylic acid derivatives or diazotization to give the corresponding biologically interesting 1,2,4-triazolo- or tetrazoloperimidines [8]. In the present note, we wish to report the reaction of **2** with a representative 1,3-dielectrophile, acetylacetone. Owing to the presence of 1,2- and 1,4-dinucleophilic centers in molecule, **2**, when treated with acetylacetone, might afford either 2-(3,5-dimethyl-1-pyrazolyl)perimidine (**4**) via a [2 + 3] cyclization or 3,5-dimethyl-1*H*-1,2,4-triazepino[4,3-*a*]perimidine (**5**) via a [4 + 3] condensation.



The reaction was performed simply by refluxing an equimolar quantity of the two reactants in absolute ethanol. It gave the condensation product together with a trace amount of a more polar intermediate **3**, which was detected only on the thin layer plate and easily eliminated by passing through a silica gel column and eluting with *n*-hexane. The pure substance was obtained as yellow needle crystals and gave consistent elemental analytical data for both structures **4** and **5**. In the infrared spectrum, it show-

ed the characteristic NH, C=N and C=C stretching bands at 3370, 1610 and 1590 cm^{-1} , respectively. In the nuclear magnetic resonance spectrum, two sharp singlets corresponding to the protons of methyl groups were found at δ 2.26 and 2.62 ppm and a singlet due to methine proton along with a multiplet for the six aromatic protons were observed at δ 6.18 and 6.70-7.15 ppm, while the deshielded broad flat NH signal appeared in more lower field at δ 10.75 ppm. Since similar values have been obtained from the condensates of analogous heterocyclic hydrazines and acetylacetone and indiscriminately claimed for both pyrazole and triazepine ring systems in the literature [9-12], mass spectral fragmentation of the product was further examined. The mass spectrum was characterized mainly by the presence of a prominent base peak corresponding to the molecular ion at m/e 262 followed by an intensive ion peak of perimidine nucleus at m/e 166 after breakdown of the dimethylpyrazole fragment (m/e 95) and loss of a hydrogen atom. The perimidine ion underwent further cleavage to give $\text{C}_{10}\text{H}_6\text{N}$ at m/e 140 and C_6H_{10} at m/e 126, while dimethylpyrazole ion was further disintegrated to C_5H_7 (m/e 67) and nitrogen or to $\text{C}_2\text{H}_3\text{N}_2$ (m/e 55) and $\text{C}_2\text{H}_2\text{N}$ (m/e 40). Significantly, no trace of triazepine ion (m/e 121) or pyridazine ion (m/e 107) could be visualized as they should arise from condensed triazepine fragmentation [10].

Based on the evidence of the mass fragmentation pattern together with the ir and nmr spectral findings, it is reasonable to assign the structure of the product from the above condensation as 2-(3,5-dimethyl-1-pyrazolyl)perimidine (**4**). Furthermore, similar condensation products were also isolated from the reaction of other 2-hydrazino-heterocycles with acetylacetone under similar conditions. The results will be reported subsequently elsewhere.

EXPERIMENTAL

2-Mercaptoperimidine (**1a**).

Compound **1a** was prepared from 8.0 g (0.05 mole) of 1,8-diaminophthalene and 3.6 ml (0.06 mole) of carbon disulfide [1], yield 9.5 g (95%), mp 265° dec.

2-Methylthioperimidine (**1b**).

A mixture of 2.0 g (0.01 mole) of **1a**, 2.8 g (0.02 mole) of methyl iodide and 100 ml of methanol was refluxed for 2 hours, then concentrated under reduced pressure and allowed to stand at 4° over night. The precipitate was filtered with suction, washed with ethanol and recrystallized from a mixture of methanol and dimethylformamide to yield 3.0 g (88%) of greenish glittery hydroiodide, mp > 300°; uv (methanol): λ max (log ϵ) 227 (4.68), 329 (4.12) nm; λ min (log ϵ) 280 (3.54) nm; ir (potassium bromide): 3210 (N-H), 2900, 2820 (=C-H), 1610, 1580 (C=N/C=C), 1325 (C-N), 670 (C-S), cm^{-1} ; ms: (70 eV), m/e 215 (M-I, 18), 214 (M-HI, 100), 199 (214-CH₃, 11), 167 (214-SCH₃, 60), 140 (167-HCN, 38), 128 (HI, 38), 127 (I, 24), 126 (C₁₀H₆, 10).

Anal. Calcd. for C₁₂H₁₀N₂S·HI: C, 42.12; H, 3.24; N, 8.19; S, 9.37. Found: C, 42.43; H, 3.22; N, 7.75; S, 9.54.

2-Hydrazinoperimidine (**2**).

A solution of 6.0 g (0.03 mole) of **1a** or 6.4 g (0.03 mole) of **1b** in 44 ml (0.09 mole) of 80% hydrazine hydrate was heated under reflux for 8 hours and after cooling the solid product was collected on a filter, washed with methanol and then recrystallized from a mixture of dimethylformamide and water to give 4.9 g (82%) of light violet crystals, mp 188-191°; ir (potassium bromide): 3340, 3260, 3050 (N-H), 2880 (=C-H), 1595, 1430 (C=N/C=C), 1330 (C-N) cm^{-1} ; nmr (DMSO-d₆): δ (ppm) 3.33 (s, NH₂), 6.44-7.12 (m, 6H, aromatic); ms: (70 eV), m/e 198 (M⁺, 18), 155 (M-CH₃N₂, 24), 140 (155-NH, 40), 126 (C₁₀H₆, 42), 43 (CH₃N₂, 80), 28 (N₂, 100).

Anal. Calcd. for C₁₁H₁₀N₄: C, 66.65; H, 5.09; N, 28.26. Found: C, 66.61; H, 5.28; N, 27.87.

2-(3,5-Dimethyl-1-pyrazolyl)perimidine (**4**).

To a solution of 2.0 g (0.01 mole) of **2** in 40 ml of absolute ethanol was added dropwise 1.2 g (0.012 mole) of acetylacetone. The reaction mixture was heated under reflux for 5 hours and then ethanol was eliminated under reduced pressure. The crude product was purified by passing

through a silica gel column using *n*-hexane as eluent and recrystallizing agent to give 1.9 g (73%) of yellow needle crystals, mp 143-145°; uv (methanol): λ max (log ϵ) 234 (4.54), 257 (4.42), 333 (4.15) nm; λ min (log ϵ) 245 (4.34), 280 (3.21) nm; ir (potassium bromide): 3370 (N-H), 2960, 2910 (=C-H), 1610, 1590 (C=N/C=C), 1350, 1260 (C-N) cm^{-1} ; nmr (DMSO-d₆): δ (ppm) 2.26 (s, N=C-CH₃), 2.62 (s, N-C-CH₃), 6.18 (s, =CH-), 6.70-7.12 (m, 6H, aromatic), 10.76 (s, NH); ms: (70 eV), m/e 262 (M⁺, 100), 166 (M-C₅H₇N₂, 30), 140 (166-CN, 31), 126 (C₁₀H₆, 20), 95 (C₃H₄N, 30), 67 (95-N₂, 20), 55 (95-C₃H₄, 70), 40 (C₃H₄, 30), 28 (N₂, 25).

Anal. Calcd. for C₁₆H₁₄N₄: C, 73.26; H, 5.38; N, 21.36. Found: C, 72.89; H, 5.43; N, 21.26.

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